

## RADIOCARBON IMPACT ON A NEARBY TREE OF A LIGHT-WATER VVER-TYPE NUCLEAR POWER PLANT, PAKS, HUNGARY

R Janovics<sup>1,2</sup> • Z Kern<sup>3,4</sup> • D Güttler<sup>5</sup> • L Wacker<sup>5</sup> • I Barnabás<sup>6</sup> • M Molnár<sup>1</sup>

**ABSTRACT.** Tree-ring series were collected for radiocarbon analyses from the vicinity of Paks nuclear power plant (NPP) and a background area (Dunaföldvár) for a 10-yr period (2000–2009). Samples of holocellulose were prepared from the wood and converted to graphite for accelerator mass spectrometry (AMS) <sup>14</sup>C measurement using the MICADAS at ETH Zürich. The <sup>14</sup>C concentration data from these tree rings was compared to the background tree rings for each year. The global decreasing trend of atmospheric <sup>14</sup>C activity concentration was observed in the annual tree rings both in the background area and in the area of the NPP. As an average of the past 10 yr, the excess <sup>14</sup>C emitted by the pressurized-water reactor (PWR) NPP to the atmosphere shows only a slight systematic excess (~6‰) <sup>14</sup>C in the annual rings. The highest <sup>14</sup>C excess was 13‰ (in 2006); however, years with the same <sup>14</sup>C level as the background were quite frequent in the tree-ring series.

### INTRODUCTION

Trees intake carbon mostly from atmospheric CO<sub>2</sub> uptake via photosynthesis. The actual radiocarbon isotope ratio of the surrounding air is preserved in their organic materials (Levin et al. 1985). In contrast to several wood compounds (lignin, resins, waxes, etc.), cellulose is not remobilized in tree tissues after formation (Hertelendi and Csongor 1982; Hua et al. 1999). Therefore, changes in the atmospheric <sup>14</sup>C activity concentration are preserved in the cellulose of tree rings (Tans et al. 1979; Otlet et al. 1989; Isogai et al. 2002; Mazeika et al. 2008).

<sup>14</sup>C emitted during the operation of nuclear facilities may increase the <sup>14</sup>C content of the local atmosphere. In several published cases, excess <sup>14</sup>C was measurable in the annual rings of nearby trees (Dai et al. 1992; Stenström et al. 1996; Mazeika et al. 2008). The Paks nuclear power plant (NPP) has been operating with VVER-440/213 type reactors since 1987. VVER-type nuclear power plants emit <sup>14</sup>C in the form of CO<sub>2</sub> and hydrocarbons. A significant part of the emission occurs in the form of hydrocarbons that are oxidized later to CO<sub>2</sub> in the atmosphere (Veres et al. 1995; Uchirin et al. 1998). In 2000–2005, the mean normalized yearly emission rates from the Paks NPP were 740 GBq for hydrocarbons and 50 GBq for CO<sub>2</sub> (Molnár et al. 2007). The power plant emits <sup>14</sup>C mainly via the 130-m-high stacks. <sup>14</sup>C concentration of air in the stacks varied between 80 and 200 Bqm<sup>-3</sup>. Several atmospheric <sup>14</sup>C samplers have been installed to monitor the air around the NPP and Interim Spent Fuel Storage Facility (ISFSF). A small excess <sup>14</sup>C (5–15‰ from <sup>14</sup>CO<sub>2</sub>) has been observed at the A4 environmental monitoring station (Figure 1) near the NPP in the prevailing wind direction. Furthermore, there was a serious third-level incident (INES-3, on the basis of International Nuclear and Radiological Event Scale [INES]) on 10 April 2003 in Unit 2 of the Paks NPP. The incident was caused by some damaged and overheated nuclear fuel in the cleaning tank (Aszódi et al. 2010). More than 10<sup>14</sup> Bq of noble gas and other radioactive gases were released to the environment through the Unit 2 stack (Hungarian Atomic Energy Agency 2003). The aim of our research is to determine whether the effect of the incident can be detected in the nearby vegetation during normal operation intervals and after the malfunction period in 2003.

<sup>1</sup>Institute for Nuclear Research of the Hungarian Academy of Sciences.

<sup>2</sup>Corresponding author. Email: janovics@atomki.hu.

<sup>3</sup>Climate and Environmental Physics, Physics Institute, University of Bern and Oeschger Centre for Climate Change Research, Bern, Switzerland.

<sup>4</sup>Institute for Geology and Geochemistry, MTA Research Center for Astronomy and Earth Sciences, Budapest, Hungary.

<sup>5</sup>Laboratory of Ion Beam Physics, ETH Zürich, Switzerland.

<sup>6</sup>Public Limited Company for Radioactive Waste Management, Hungary.

## EXPERIMENTAL

### Description of Sampling Area and Sample Handling

Sampling sites were located near the Paks NPP and the background control site at Dunaföldvár. Paks NPP is situated near the Danube River in southern Hungary (46°35'N, 18°51'E) (Figure 1). The background sampling point (station B24) is surrounded by an agricultural field near the outskirts of Dunaföldvár, 25 km north of Paks NPP (46°46'N, 18°56'E). The dominant wind direction at B24 is from the northwest. Thus, the atmospheric  $^{14}\text{C}$  level at B24 should not be influenced by Paks NPP (Molnár et al. 2007).

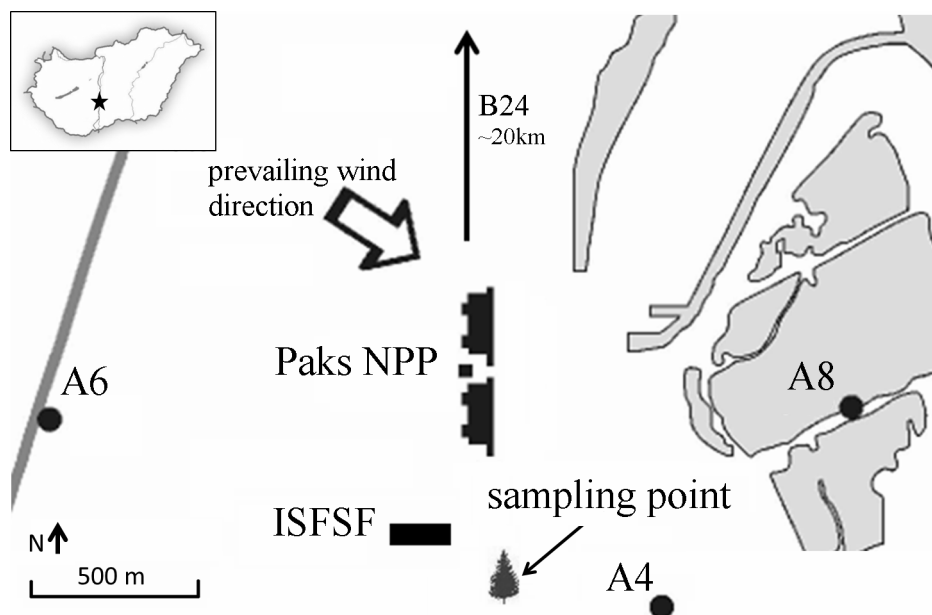


Figure 1 Map of the sampling area: A4, A6, and A8 are the environmental monitoring stations; NPP: Paks nuclear power plant; ISFSF: Interim Spent Fuel Storage Facility.

Sampling was carried out in October 2010 at the end of the local growing season. Samples were collected from 400 m south of the power plant and 250 m southeast from the ISFSF. Healthy Scots pine (*Pinus sylvestris* L.) trees were selected for sampling. Despite the fact that pine is not an indigenous species in the area, this conifer was selected because evergreen species are better biomonitors for airborne pollution due to their larger leaf area and permanent foliage (Cutter and Guyette 1993). Multiple cores (5–6) were extracted from selected trees using an increment borer (Haglöf®) (Figure 2). The sampling height was the standard breast-height. Increment cores were slightly trimmed perpendicular to fibers using a Teflon®-coated razor blade. First, tree-ring sequences extracted from the same tree were carefully cross-checked under a binocular microscope, then samples from different trees were compared (Stokes and Smiley 1968). A LINTAB digital-positioning table and TSAP Win 0.55 software (Rinn 2005) were used to measure the annual ring widths with a precision of 0.01 mm, as well as for cross-dating the growth series by graphical comparison against each other. The results were checked for missing rings and dating errors using COFECHA software (Holmes 1983). Finally, tree rings from each core were detached using a scalpel, inspected under a binocular microscope, and subsamples belonging to the same annual increment were pooled. Cross-

dating and tree-ring separation were done by a trained dendrochronologist using the facilities of the Budapest Tree-ring Laboratory (Eötvös University, Dept. of Palaeontology; Kázmér and Grynaeus 2003).

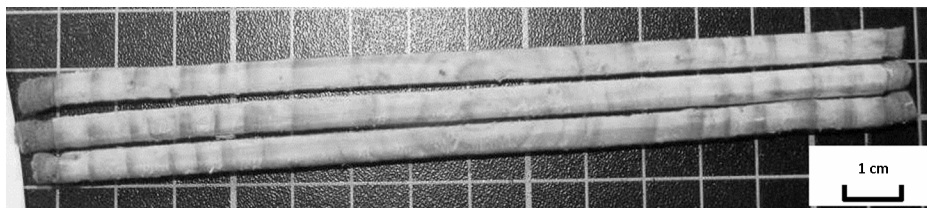


Figure 2 A set of increment cores extracted from a *Pinus sylvestris* specimen before ring separation

In order to remove disturbing wood compounds, the  $\alpha$ -cellulose was prepared from annual rings at the ETH Zürich. The annual rings from 2000 to 2009 were chopped into small pieces. Preparation was performed according to the BABAB (base-acid-base-acid-bleaching) method (Němec et al. 2010). As a first step, the sample was soaked in 4% NaOH overnight. The samples were then treated with 4% HCl for 1 hr. The third step was soaking in 4% NaOH for 1.5 hr again and a final soaking in 4% HCl for 1 hr. Between each step, samples were heated to 75 °C and rinsed to neutral with demineralized water. After the last washing step, 5% NaClO<sub>2</sub> was added to bleach the samples and samples were acidified to pH 2 with HCl. Bleaching was done for several hours until the cellulose was pure white (Němec et al. 2010; Gaudinski et al. 2005). After the bleaching process, the sample was washed to pH 4, and dried at 75 °C in an oven. All of chemical agents used were of analytical grade.

#### Graphitization and AMS Measurement

The dried holocellulose samples were graphitized by an EA-AGE (Elemental Analyser coupled with Automatic Graphitisation Equipment). CO<sub>2</sub> gas generated from combustion by the EA is adsorbed on the zeolite trap of the AGE and is then flushed into the reaction cell. Based on the sample amount, the AGE automatically doses the proper quantity of H<sub>2</sub> gas and graphitizes the sample (Wacker et al. 2010a). The <sup>14</sup>C measurements were performed with the MICADAS AMS at ETH Zürich (Synal et al. 2007; Wacker et al. 2010b). Measurement time and conditions were set to collect at least 500,000 net counts for every single target and the NPP and B24 background tree-ring pairs followed each other in the same sample magazine. The overall measurement uncertainty for each sample was below 3‰, including normalization, background subtraction, and counting statistics.

#### RESULTS AND DISCUSSION

The measurement results are given in Table 1 and were corrected for decay of the standard and for  $\delta^{13}\text{C}$ , calculated to the year of formation of the given tree rings as described by Stuiver and Polach (1977). The <sup>14</sup>C activity concentration of the tree rings at both sampling points decreased by more than 44‰ in the course of the investigated period as a result of the decline of the <sup>14</sup>C signal due to atmospheric nuclear testing. The <sup>14</sup>C atmospheric concentration has been continuously decreasing almost exponentially following the Comprehensive Test Ban Treaty because of the buffering effect of the biosphere and the oceans (Levin et al. 1985; Povinec et al. 1986; Hua et al. 2000; Levin and Kromer 2004; Mazeika et al. 2008).

The decrease in atmospheric <sup>14</sup>C concentration can be described by an exponential function (Hua et al. 1999; Rakowski et al. 2010). Results from tree-ring series of Paks NPP and the background station also fit well on an exponential curve, with correlation coefficients of 0.95 and 0.96, respectively.

Table 1  $^{14}\text{C}$  activity values of pine tree rings at the B24 (background) and Paks NPP locations ( $\pm 3\text{‰}$ ;  $1\sigma$ ).

Origin year of tree rings	B24 (‰)	Paks NPP (‰)	Paks NPP–B24 (‰)
2000	86	87	1
2001	79	85	6
2002	71	77	6
2003	68	74	6
2004	59	67	8
2005	54	53	–1
2006	45	58	13
2007	45	50	5
2008	40	51	11
2009	42	42	0

There is no significant  $^{14}\text{C}$  excess in 3 different years of the decade studied (2000, 2005, and 2009). The sample from Paks appears to have been planted in a nursery garden far from Paks NPP during the first couple of years after germination. The innermost ring from the increment core (2000) extracted at breast height might represent the last year of this juvenile growing period. For this reason, the data of the first year (2000) were ignored from the NPP impact study. The reason for the very low NPP effect in 2005 and 2009 is not clear. Between 2009 and 2010, the  $^{14}\text{C}$  concentrations of the tree rings near Paks NPP were slightly, but systematically, higher by  $5.5 \pm 1.4\text{‰}$  than the samples taken at the background sampling site at Dunaföldvár.

In Molnár et al.'s (2007) study, air samples were taken at the A4 atmospheric  $^{14}\text{C}$  sampling station during the vegetation period (April–October). Between 2000 and 2005, the average  $^{14}\text{C}$  excess in the  $\text{CO}_2$  fraction was  $12 \pm 5\text{‰}$ , while for the total carbon fraction, including hydrocarbons, the excess was  $\sim 67\text{‰}$ . The observed significantly lower effect in the tree rings probably means that  $^{14}\text{C}$  emitted mostly in the form of hydrocarbons by the NPP, and is only incorporated to a very limited extent into the tissues of the nearby trees in the vicinity of the NPP.

The highest excess  $^{14}\text{C}$  concentrations were observed in 2006 and 2008, when the excess  $^{14}\text{C}$  concentration in the Paks tree rings slightly increased ( $\sim 12\text{‰}$ ) compared to the background (Figure 3). These values are almost twice as high as the average of the other values. However, the effects of a cleaning tank incident of Paks NPP in 2003 were not seen in the tree rings investigated.

The tree-ring  $^{14}\text{C}$  data are compared with the atmospheric  $^{14}\text{C}$  values of the Jungfraujoch mountain station (Levin et al. 2008) in Figure 4. Levin's data are measured values between 1986 and 2007, but have extrapolated monthly values up to 2009. In order to correct for the growth period of a pine tree, Levin's data from the months April to October in each year were averaged and plotted (see Figure 4). The tree-ring  $^{14}\text{C}$  values were always close to the Jungfraujoch curve obtained for the productive period of the vegetation cycle. In most cases, the tree-ring-derived values at the background station are the same as the Jungfraujoch atmospheric  $^{14}\text{C}$  data, while those from the vicinity of Paks NPP are generally above the Jungfraujoch curve. The average excess of the tree from B24 to the Jungfraujoch air  $^{14}\text{C}$  is less than  $2\text{‰}$ , while for the NPP tree it is  $7 \pm 1\text{‰}$ .

### *<sup>14</sup>C Impact in a Nearby Tree of Paks NPP*

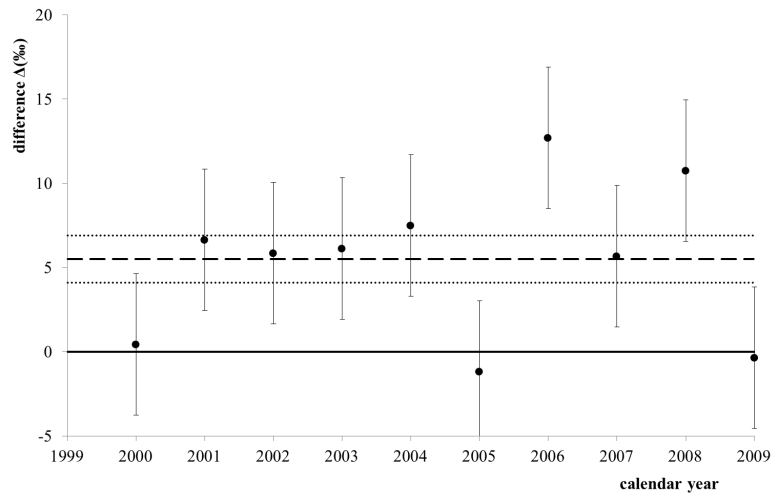


Figure 3 Change in excess  $^{14}\text{C}$  concentration for tree rings at Paks NPP (continuous line at zero shows the background level, dashed line and dotted lines shows the average excess and the uncertainty band, respectively.)

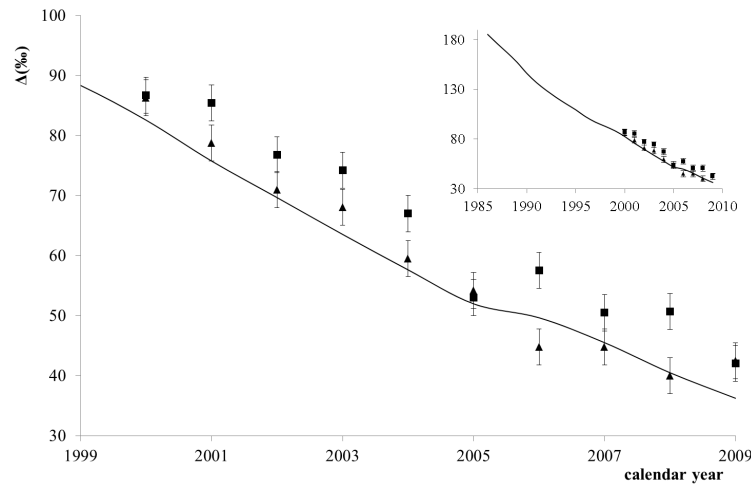


Figure 4 Change in  $^{14}\text{C}$  concentration for tree rings at B24 (triangles) and Paks NPP (squares) from 2000 to 2009 and fit on the decreasing trend of atmospheric  $^{14}\text{C}$  concentration at Jungfraujoch (curve) (Levin et al. 2008).

## CONCLUSION

The  $^{14}\text{C}$  concentrations of tree rings sampled near Paks NPP exceed those from the background station in most cases; however, this difference is small. The cleaning tank incident in 2003 was not observable in the tree nearby Paks NPP. Tree-ring-based environmental  $^{14}\text{C}$  reconstruction may be significant in any posterior survey of excess  $^{14}\text{C}$  emissions from NPP, even in the case of PWR power plants. The continuous global decrease of atmospheric  $^{14}\text{C}$  concentration can be observed in the tree rings of both sampling sites, and these values fit well both in order of magnitude and in comparison to the data of the Jungfraujoch atmospheric  $^{14}\text{C}$  station. The contribution of Paks NPP to the

$^{14}\text{C}$  content of the trees was on average  $5.5 \pm 1.4\%$  above background for the 10-yr period investigated. The highest  $^{14}\text{C}$  excess was  $13 \pm 4\%$  in 2006. Thus,  $^{14}\text{C}$  emitted by the NPP to the atmosphere causes only a minor increment in the  $^{14}\text{C}$  content of the annual rings of the nearby trees. This is a logical consequence of the observation that PWR-type NPPs emit  $^{14}\text{C}$  mainly in the form of hydrocarbons and not carbon dioxide.

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